

WHAT IS CLAIMED IS:

1. A thermoelectric material composed of at least one element selected from the group consisting of Bi and Sb and at least one element selected from the group consisting of Te and Se, and comprising crystal grains having respective [001] directions and an average grain size equal to or less than 30 microns, certain crystal grains having the [001] directions crossing a direction in which an electric current flows at 45 degrees or less, said certain crystal grains occupying an area equal to or less than 10 % on a section perpendicular to said direction.
2. The thermoelectric material as set forth in claim 1, in which said thermoelectric material contains at least one element selected from the group consisting of I, Cl, Hg, Br, Ag and Cu.
3. The thermoelectric material as set forth in claim 1, in which electron serves as the major carrier therein.
4. A process for producing a thermoelectric material composed of at least one element selected from the group consisting of Bi and Sb and at least one element selected from the group consisting of Te and Se, comprising the steps of:
  - a) preparing a fusion of said thermoelectric material;
  - b) rapidly solidifying said fusion so as to obtain flakes of said thermoelectric material;
  - c) stacking said flakes so as to form a lamination;

d) putting said lamination into a die unit having an inlet portion and an outlet portion obliquely extending with respect to said inlet portion; and

e) pressurizing said lamination for extruding a bulk of said thermoelectric material from said die unit at least once so that a shearing force is exerted on said lamination at a boundary between said inlet portion and said outlet portion.

5. The process as set forth in claim 4, in which said angle between said inlet portion and said outlet portion ranges from 30 degrees to 150 degrees.

6. The process as set forth in claim 4, in which an angle between said inlet portion and said outlet portion ranges from 90 degrees to 120 degrees.

7. The process as set forth in claim 4, in which said lamination is heated to 300 – 600 degrees in centigrade in said step e).

8. The process as set forth in claim 4, in which said lamination is heated to 320 – 450 degrees in centigrade in said step e).

9. The process as set forth in claim 4, in which an angle between said inlet portion and said outlet portion ranges from 30 degrees to 150 degrees, and said lamination is heated to 300 – 600 degrees in centigrade.

10. The process as set forth in claim 4, in which an angle between said inlet portion and said outlet portion ranges from 90 degrees to 120 degrees, and said lamination is heated to 320 – 450 degrees in centigrade.

11. The process as set forth in claim 4, in which said thermoelectric material has a ratio of  $T_e$  to  $S_e$  fallen within the range between 2.5/ 0.5 and 2.7/ 0.3.

12. The process as set forth in claim 4, in which said thermoelectric material has a ratio of Te to Se fallen within the range between 2.5/ 0.5 and 2.7/ 0.3, an angle between said inlet portion and said outlet portion ranges from 30 degrees to 150 degrees, and said lamination is heated to 300 – 600 degrees in centigrade.

13. The process as set forth in claim 4, in which said thermoelectric material has a ratio of Te to Se fallen within the range between 2.5/ 0.5 and 2.7/ 0.3, an angle between said inlet portion and said outlet portion ranges from 90 degrees to 120 degrees, and said lamination is heated to 320 – 450 degrees in centigrade.

14. The process as set forth in claim 4, in which a cross sectional area of said inlet portion is at least 4.5 times wider than an across sectional area of said outlet portion.

15. The process as set forth in claim 4, in which an cross sectional area of said inlet portion is at least 4.5 times wider than an across sectional area of said outlet portion, said thermoelectric material has a ratio of Te to Se fallen within the range between 2.5/ 0.5 and 2.7/ 0.3, an angle between said inlet portion and said outlet portion ranges from 30 degrees to 150 degrees, and said lamination is heated to 300 – 600 degrees in centigrade.

16. The process as set forth in claim 4, in which an cross sectional area of said inlet portion is at least 4.5 times wider than an across sectional area of said outlet portion, said thermoelectric material has a ratio of Te to ~~Se fallen~~ within the range between 2.5/ 0.5 and 2.7/ 0.3, an angle between said inlet

portion and said outlet portion ranges from 90 degrees to 120 degrees, and said lamination is heated to 320 – 450 degrees in centigrade.

17. The process as set forth in claim 4, in which said bulk of said thermoelectric material is extruded from said die unit at 0.01 - 1 mm/ min in said step e).

18. The process as set forth in claim 4, in which said bulk of said thermoelectric material is extruded from said die unit at 0.05 – 0.2 mm/ min.

19. The process as set forth in claim 4, in which said steps d) and e) are repeated at least once.

20. The process as set forth in claim 4, in which a pressure is applied to said bulk of said thermoelectric material in a direction opposite to the direction in which said bulk is extruded.

21. The process as set forth in claim 4, further comprising

f) sintering said bulk of said thermoelectric material with the assistance of plasma in inert atmosphere.

22. The process as set forth in claim 4, further comprising

f) pressurizing said bulk of said thermoelectric material in a direction perpendicular to a centerline of said outlet portion on a virtual plane defined by said centerline and a centerline of said inlet portion for a hot pressing.

23. A process for producing a thermoelectric material composed of at least one element selected from the group consisting of Bi and Sb and at least one element selected from the group consisting of Te and Se, comprising the steps of:

a) preparing one of an ingot of said thermoelectric material and a powder of said thermoelectric material;

b) putting said one of said ingot and said powder into a die having an inlet portion and an outlet portion obliquely extending with respect to said inlet portion; and

c) pressurizing said one of said ingot and said powder for extruding a bulk of said thermoelectric material from said die unit at least once so that a sharing force is exerted on said one of said ingot and said powder at a boundary between said inlet portion and said outlet portion.

24. The process as set forth in claim 23, in which said powder is prepared in said step a), and said process further comprises the steps of

d) reducing said powder in hydrogen atmosphere between said step a) and said step b), and

e) sintering said powder between said step d) and said step b) for solidifying said powder.

25. The process as set forth in claim 23, in which a pressure is applied to said bulk of said thermoelectric material in a direction opposite to the direction in which said bulk is extruded in said step c).

26. A thermoelectric module for producing a temperature difference from an electric current passing therethrough, comprising:

a pair of substrates having respective inner surfaces opposite to each other;  
conductive layers formed on said inner surfaces; and

plural thermoelectric elements of a first conductivity type and other thermoelectric elements of a second conductivity type held in contact with said conductive layers so as to be alternately connected in series,

each of the thermoelectric elements consisting of said plural thermoelectric elements and said other thermoelectric elements including a piece of thermoelectric material and metal layers,

said piece of thermoelectric material being composed of at least one element selected from the group consisting of Bi and Sb and at least one element selected from the group consisting of Te and Se,

said piece of thermoelectric material comprising crystal grains having respective [001] directions and an average grain size equal to or less than 30 microns, certain crystal grains having the [001] directions crossing a direction in which an electric current flows at 45 degrees or less, said certain crystal grains occupying an area equal to or less than 10 % on a section perpendicular to said direction.

27. The thermoelectric module as set forth in claim 26, in which said thermoelectric material contains at least one element selected from the group consisting of I, Cl, Hg, Br, Ag and Cu.